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MICROWAVE BONDING OF CERAMICS: FINAL REPORT

S.J. Oda and I.S. Balbaa

The use of microwaves to bond ceramic substrates can provide a stronger chemical bond compared to that commonly produced by conventional techniques. Good diffusion (chemical) bonding depends on the selection of appropriate microwave power levels and exposures and on the properties of both the glass powder bonding material and the ceramic substrate(s) (ie, thermal expansion coefficients, substrate porosity, etc). The most suitable adhesive consisted of a glass powder containing two microwave coupling agents: glycerol and sodium nitrate. Results from an extensive literature review, experimental procedures and results are appended.

1.0 INTRODUCTION

Advanced ceramics are gaining in importance primarily as a result of their high strength and ability to withstand heat and chemical attack. (A description of advanced ceramics is given in Appendix A.) In order to take advantage of these properties it is often necessary to bond ceramic materials to ceramic and metal substrates. For cost effectiveness, it is obviously important that any joining methods should provide reliable and satisfactory bonding in a minimum amount of time.

Conventional ceramic-ceramic and ceramic-metal bonding techniques include thermocompression, liquid-phase, eutectic, and hot isostatic pressing. A brief review of these techniques is provided in Appendix B. The strongest type of bond occurs when the bonding of 'adhesive' material diffuses into the substrate or vice versa. This type of bond generally results from the application of both high pressure (~500 MPa) and temperature (~500°C). If these conditions are not met, weaker bonding usually results.

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Using technical information gained from preliminary tests for Powerplex and work done at Los Alamos a study was initiated to investigate bonding of a representative selection of 'advanced' ceramics using microwave power.

This report summarizes the results of this study to date with conclusions and recommendations for further study. For the interested reader the report includes a number of Appendices as background information for this report:

- primer on advanced ceramics (Appendix A)
- survey of ceramic bonding (Appendix B)
- literature references and contacts (Appendix C)
- materials selection and acquisition (Appendix D)
- experimental tests (Appendix D)
- product characterization (Appendix D)

2.0 PROJECT METHODOLOGY

A review of technical literature and contacts with consultants and manufacturers were conducted to provide the necessary technical background. Appendix A summarizes this information with a primer on advanced ceramics, a brief description of current bonding techniques, a list of contacts, and technical references used during this study.

From the results of the literature review, potential materials ('adhesives' and ceramic substrates) were identified and acquired. Substrates and adhesive were placed in a microwave applicator and exposed to microwaves for a fixed time period. The resultant 'composite' (ie, composed of 2 substrates and adhesive) was inspected visually and by SEM to determine the effect of microwave heating especially at the bond interfaces. Due to difficulty in sample preparation no attempt was made to determine physical strength of the bond.

3.0 DISCUSSION OF RESULTS

Laboratory tests undertaken in this study indicate conclusively the feasibility of bonding ceramics with microwaves. Details of material selection criteria, experimental tests and characterization procedures are given in Appendix D.

The choice of the adhesive mixture is critical to the success of the bonding operation. It became clear that a mixture of at least two components is required for an acceptable bond: a coupling agent and a bonding material. Microwaves initially heat the coupling agent up to temperatures at which the bonding material itself will start to absorb microwaves. (The substrate also will start to absorb microwaves at these temperatures.) As the bonding material begins to heat to its melting point it appears to diffuse into the ceramic substrate.

The tests described in Appendix D indicate that two coupling agents are required: glycerol to initiate heating up to 300°C where sodium nitrate, the second coupling agent, starts to couple with microwaves. As a result, the glass powder in the adhesive mixture is heated and begins to absorb microwaves up to its melting point. The use of only one of these coupling agents did not provide sufficient thermal energy to melt the glass powder.

The tests also indicated the importance of the ratio of components in the adhesive mixture. A 1:1:1 weight ratio of the two coupling agents and glass powder provided the most promising results. Excessive heating occurred when the amount of either coupling agent was increased. Decomposition of the glass powder and entrapment of evolved gases in the cooled glass was observed. When the amount of coupling materials was reduced, the high temperatures required for diffusion bonding were not attained. In both cases, weaker bonds resulted.

The selection of an acceptable glass powder depends on two factors: melting point and coefficient of thermal expansion. For an acceptable bond, the melting point of the glass powder should be lower than that of the substrate and the coefficients of thermal expansion for glass powder and substrate should be similar. In the latter case, tests indicated that a difference of 20% between thermal expansion coefficients still produced acceptable diffusion bonding. At differences of 50%, cracks in the bonding phase were observed. This observation could prove useful when bonding substrates with different expansion coefficients. An acceptable bond could result by selecting a bonding material with an expansion coefficient between that of the two substrates. As a result of the diffusion bonding, the final properties of the substrates and bonding material will change. Additional testing is required to quantify the changes in these properties.

The effect of microwave power exposure used in ceramic bonding is important. It was observed that the best results were obtained by positioning the sample in the centre of a multimode microwave applicator (internal dimensions of 45 x 45 x 45 cm^3) about 8 cm above the bottom. Absorbed microwave power was approximately 700 W and test duration was between 5-10 min. Indeed longer exposures appeared to create excessive heating and melting of some of the ceramics.

Tests in the microwave applicator indicated that sample size affected the rate of heating. It was expected that, as the sample size increased, more microwave power would be required to initiate heating. However, the experimental results revealed a different behaviour. Less microwave power was required to initiate heating in samples up to a particular size, or more appropriately, ratio of sample size to applicator volume. Above this ratio, the samples behaved in a more conventional manner (i.e., more power was required with increasing sample size).

4.0 SUMMARY

1. A comprehensive literature review and contacts with consultants and ceramic manufacturers were made to gather relevant information on ceramic-ceramic bonding for this study (Appendices A, B and C).

2. Several 'adhesive' mixtures were exposed to microwaves. These mixtures included: different amounts of glass powder, sodium nitrate and glycerol. In some cases glass and beta-alumina powder mixtures were tested.

3. Two glass powders were used in the tests: soda lime with a melting point near 1100°C and two solder glasses with softening temperatures of ~375°C. The properties of these glasses are given in Appendix D.

4. Several ceramic substrates were used for the bonding tests including: porcelain, beta-alumina, magnesia, high purity (96% and 99%) alumina and mullite.

5. Scanning electron microscopy (SEM) was the main characterization tool. It provided the following information:

   (a) Chemical analysis at various locations in the ceramic-ceramic sample.

   (b) Micrographs of the bond area.

   (c) Mapping of specific atomic elements at the ceramic-bond interface.

5.0 CONCLUSIONS

1. The tests conducted in this study demonstrate the feasibility of using microwave to bond ceramics.

2. For suitable bonding, the type of adhesive should have a thermal expansion coefficient close to that of the ceramic substrates to be bonded.

3. The most suitable bonding adhesive consisted of two microwave coupling agents (glycerol and sodium nitrate) together with a glass powder. The ratio of these components needs to be adjusted for optimum bonding.

4. Good diffusion bonding depends both on appropriate microwave power levels and the properties of glass powder and ceramic substrates (ie, substrate porosity, thermal expansion coefficients). Size and aspect ratio of substrates are also important considerations when bonding with microwaves.

5. Different microwave power levels and exposure periods are required to bond different ceramics.

6.0 RECOMMENDATIONS

1. Additional tests are recommended to (a) examine the effect of adhesive thickness on the bond properties and (b) optimize the microwave power required to bond thin ceramic materials with surface areas larger than 1 cm^2.

2. The properties for ceramic bonding will depend on the specific end-use. On the basis of successful laboratory tests, it is recommended that two applications be investigated to determine whether suitable bonding of 'real-life' materials is technically feasible.

3. The possibility of bonding ceramics by microwaves without the use of adhesives should be examined.

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APPENDIX A

ADVANCED CERAMICS

Ceramic Materials

The term 'ceramic' applies to a variety of inorganic materials from coarse fire brick to glass. An acceptable definition of ceramics is "an inorganic, non-metallic material processed or consolidated at high temperatures"/4/. These materials can be divided into two main categories: traditional and advanced (aka fine, engineering, technical, structural, etc). The main difference between traditional and advanced ceramics is the nature of the bonds between the ceramic particles or grains. With advanced ceramics, manufacturing techniques and carefully controlled alloying, result in 'self-bonding' of most particles. 'Self-bonding' means that the ceramic grains are joined at grain boundaries by the same energy equilibrium mechanisms that bond metal grains together. With traditional ceramics, the grains are joined together by a 'ceramic bond' that represents a weaker mechanical linking or interlocking of particles. In general, the impurities in traditional ceramics prevent the particles from self-bonding.

Traditional Ceramics

Traditional ceramics, also sometimes called clay or silicate products, can be classified as follows: whitewares (ie, pottery, dinnerware, sanitaryware), heavy clay products (brick, terra cotta, sewer pipe, drain tile), refractories (alumina products, silica brick, silicon carbide), glasses and enamels. The three main raw materials used in making traditional ceramics are clay (ie, kaolinite, bentonite), feldspar (spar), and sand (flint).

Advanced Ceramics

Advanced ceramics with "superior mechanical, thermal, electrical, chemical and optical properties" are being used for automobile engine components, wear- and corrosion-resistant parts for industrial equipment, opto-electronics for communication, and sensors for detection and control applications.

Advanced ceramics can be fitted into three basic categories: ceramic oxides, glass-ceramics, and carbides and nitrides.

(i) Ceramic Oxides

There are three main metal oxides which are used as the primary constituent of a ceramic. These are alumina, beryllia, and zirconia.

The alumina ceramics are used in steady state high temperature applications (up to 1800°C). The poor resistance of the aluminas to thermal shock require gradual temperature changes.

The aluminas are also susceptible to corrosion from strong hydrofluoric acids, steam, and sodium.

Beryllia ceramics dissipate heat well and are a good electrical insulator. Beryllia has excellent thermal shock resistance, and a low thermal coefficient of expansion.

Zirconia is used primarily for its extreme inertness to most metals. Zirconia ceramics retain their strength up to 2200°C which is the highest of all the ceramics. Zirconia ceramics are commonly used for bricks and crucibles.

Other oxides used include CaO, SiO_2, MgO, ThO_2, TiO_2 and mullite (Al_2O_3 - SiO_2).

(ii) Glass-Ceramics

Glass-ceramics are composed of several oxides that form complex multiphase microstructures. They are called glass-ceramics because parts made from these materials are formed from molten glass and subsequently crystallized. The major applications for glass-ceramics are cooking vessels, tableware, and smooth cooktops.

A popular glass-ceramic is Corning's Macor, which is a machinable glass-ceramic. Macor is approximately as strong as alumina and has many of the high temperature and electrical properties of the glass-ceramics. The main advantage of Macor is that it can be machined with conventional tools.

(iii) Carbides and Nitrides

Boron carbide is noted for its very high hardness and low density. These characteristics qualify this ceramic for light weight, bullet-proof armor plate. The material has the best abrasion resistance of any ceramic, so it is also specified for pressure-blasting nozzles and similar high-wear applications. A limitation of boron carbide is its low strength at high temperatures.

Boron nitride is noted for thermal shock resistance, corrosion resistance, high temperature strength, electrical resistance, and high thermal capacity. Applications for boron nitride include furnace tooling, nozzles, insulators, bearings, and high temperature construction materials.

Depending on the manufacturing process, the properties of silicon nitride are high strength at high temperatures, excellent thermal shock resistance, low density, little dimensional change in processing, and excellent wear characteristics. Silicon nitride ceramics are used for thermocouple sheaths, torch nozzles, furnace hardware, and crucibles.

Silicon nitride is stronger than silicon carbide up to about 1500°C, but at about 1150°C, silicon nitride grain boundaries soften, or "creep", and strength drops. Above 1500°C, silicon carbide is the stronger ceramic.

In general, silicon nitrides and silicon carbides are the strongest structural materials for high temperature, oxidation-resistant service.

Other carbide ceramics include TiC, WC, TaC, NbC, HfC, ZrC, and VC.

Other nitride ceramics include AlN, BN, Be_3N_2, ZrN, NbN, VN, and TiN.

APPENDIX B

SURVEY OF CERAMIC BONDING

Although microwave bonding of ceramics has only been studied recently, bonding/sealing of ceramics to ceramics, and ceramics to metals has received considerable study in North America, Japan, and Europe.

The following methods have been used to bond ceramics to ceramics:

1. Inserting SiC powder between ceramic surfaces and carrying out an isostatic press treatment at a temperature of 1600-2200°C (Japanese patent no. 84185/83).

2. Apply a paste (prepared from CuS, $LaCrO_3$, and SiO_2 powders with an organic solvent) to the ceramic surface and heat to 1000-1200°C (Japanese patent no. 75976/80).

3. Joining silicon nitride ceramics by inserting a layer of oxide, nitride, or carbide of a metal between the surfaces (and although not stated, it is assumed the surface is heated to an appropriate temperature) (Japanese patent nos. 88184/83, 93402/74, 130865/80, and 79876/83).

4. Apply a "decomposed" organic compound to the surfaces and heat to an appropriate temperature. Bond is formed from diffusion of carbon into the surfaces. The effects that the temperature, and load on the sample during the processing have on the sample's flexural strength are shown in reference 5.

5. Apply an "alloy" (liquid solution containing titanium or zirconium) to the ceramic surfaces and in a vacuum oven, heat to 600°C for 15 minutes and then allow to cool to 200°C before being gas cooled/6/.

6. Apply an "active metal sealing layer" ($X_xTi_yZr_z$, where X is a metal with melting temperature between 950 and 1350°C) to the surfaces of the ceramics, press the surfaces together, and in a vacuum oven heat the samples to 950-1350°C/7/.

7. Apply a slip or paste with the same composition as the ceramic parts and heat to a high temperature (usually >1600°C)/8/.

8. Apply a slurry containing powdered "solder glass" (melting temperatures between 400°C to 1100°C), an organic compound and an oxidizing agent, and heat in a microwave applicator to the melting temperature of the glass/2,3/.

APPENDIX C

REFERENCES

1. Computer Literature Search

A computer literature search was performed to provide current technical references on ceramics bonding (see Appendix A). Using the library services at OHRD (April 22/86) the following databases were searched:

- National Technical Information Service: 1964-86/ISS09
- Compendex: 1970-86/April
- EI Engineering Meetings: 1986/April
- Inspec: 1977-86/ISS10
- SCISEARCH: 1984-86/wk 12
- Chemical Abstracts: 1967-86 UD = 10414
- World Wide Patents Index, (latest 1981+)
- World Wide Patents Index, (1963-1980)

2. List of Contacts:

Organization/Company	Contact
1. Canadian Ceramic Society 2175 Shepherd Ave E Suite 110 Willowdale, Ontario Tel: 491-2886	N. Gariffe
2. Johns Scientific (dist. Corning Macor) 175 Hanson Street Toronto, Ontario Tel: 699-5555	Jack Turner (sales rep)
3. Owens-Illinois Inc - Kimble Div One Seagate Toledo, Ohio Tel: (419) 247-5000	Bob Montgomery (sales rep) Perry Pirooz (technical asst)

4. Thermalloy Corporation
   57 Glen Cameron Rd, Unit 21
   Thornhill, Ontario
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5. EYC Technical Ceramics Inc
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   P.O. Box 250
   Espanola, Ontario
   Tel: (705) 869-4566

   Bob McEwen
   (proj mgr)

6. Los Alamos National Laboratory
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   Los Alamos, New Mexico 87545

   Thomas Meek

7. Alcan Research Laboratories
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   Kingston, Ontario
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8. Industrial Ceramics Ltd
   473 Hensall Circle
   Mississauga, Ontario
   Tel: 276-5447

   Jim Foster

9. Home Technics Ltd
   624-646 Neal Drive
   P.O. Box 1678
   Peterborough, Ontario
   Tel: (705) 748-3387

   Karl Kappes

10. Almax Industries Ltd
    61 Needham Street
    Lindsay, Ontario
    Tel: (705) 324-5100

    Kamal El Assal

References

Following is a list of references that were selected from the literature search:

1. Blake, R.D., Meek, T., "Ceramic-Ceramic Seals by Microwave Heating", submitted to Journal of Materials Science, 1985.

2. Blake, R.D., Meek, T., "Sodium Nitrate Containing Mixture for Producing Ceramic-Glass -Ceramic Seal by Microwave Heating", US Patent #659586 (database NTIS).

3. Blake, R.D., Meek, T., "Ceramic-Glass-Metal Seal by Microwave Heating", US Patent #4529857.

4. Murthy, M.K., "Advanced Ceramics - Technology Situation Report", draft report for the Department of Regional Industrial Expansion (Office of Industrial Innovation), September 1985.

5. Okamura, H., Akiyama, H., Kamoshita M., Miyasaki, K., "Ceramic composite article and process for the production thereof", pub. #0146321, appl. #843085325 European Patent Application, Dec 7/84 (database - ChemAbs).

6. Hepburn, W.D., "Sealing Ceramic to Ceramic or to Metal", UK Patent Application #GB 2114040A (database - ChemAbs).

7. Killey, N.M., "Improvements in or Relating to Ceramic-to-Metal and Ceramic-to-Ceramic Seals", International Patent #1249417, published Oct 13/71.

8. Hauth, W.E., "Ceramic-to-Ceramic Sealing of Large Shapes", American Ceramic Society Bulletin, June 1979, pg 584-6 (database - EI Engineering Meetings).

9. Elssner, G., Dien, W., Wallace, J.S., "Microstructure and Mechanical Properties of Metal-to-Ceramic and Ceramic-to-Ceramic Joints", Materials Science Research V 14, 1981 (database NTIS).

10. Shimada, M., Suganama, K., Okamoto, T., Koizumi, M., "Diffusion Bonding of Ceramics-Ceramics and Ceramic-Metal under Pressure", Materials Science Monographs 28B, 1985 (database - ChemAbs).

11. Klein, A.J., "Processing with Microwaves", Advanced Materials & Processes" pgs 36-9, December 1985.

12. Machine Design - Materials Reference Issue, April 17, 1986.

APPENDIX D

EXPERIMENTAL PROCEDURE

(a) Materials Selection

Substrates

The representative substrates used in this project were mullite ($3Al_2O_3.2SiO_2$) and two different grades of alumina (Al_2O_3). The relevant properties are shown in Table D1.

It was decided to limit the evaluation to three alumina substrates to enable a reasonable comparison bonding characteristics. Of particular importance is the effect of thermal expansion coefficients on bonding the ceramic substrates. Alumina substrates were selected primarily because of their common use in a wide variety of applications including thermal and electrical insulation, electronics, packaging and most recently, as engine components. Porcelain, beta-alumina and magnesia substrates were also used in preliminary tests.

Bonding Adhesives

The bonding adhesive used in the study contained two main ingredients: a microwave coupling agent and a bonding material. The coupling agent is a good absorber of microwaves so that it is used to heat the bonding material. In this case the coupling agent can function in two ways. Firstly, if the bonding material is transparent to microwaves, the coupling agent can be used to indirectly heat the bonding material. In the second case, the coupling agent heats the bonding material up to a temperature at which the bonding agent itself will absorb microwaves.

Several coupling agents can be used at one time. In this study, water, sodium nitrate and glycerol were used in varying proportions. Water assists coupling microwaves up to 100°C; glycerol up to ~300°C and sodium nitrate is an excellent microwave coupling agent over 200°C.

A glass frit (or powder) was selected for the laboratory evaluations. Two types of frit were selected for the tests: a soda lime glass (softening point ~730°C) and a 'low' softening point glass (softening point 370°C). Table D2 outlines the relevant properties of the frits. In addition, because of its excellent coupling with microwaves, β-alumina powder was also used in some preliminary tests as a coupling/bonding material.

In order to screen the bonding materials, a variety of powder mixtures and coupling agents were heated in a multimode microwave applicator. Heating tests were conducted under similar conditions: ~2 g samples were placed in insulated porcelain crucibles at a location of highest microwave power. The samples were exposed for five minutes to microwave of ~1000 W. Table D3

summarizes the results.

Bonding Tests

From the materials in Table D3, microwave heating trials were performed by placing the most promising adhesives between ceramic disks (electrical grade porcelain) to see whether a bond could be produced. Results of these tests are summarized in Table D4. It should be noted that the reference to bond quality refers to the bond between the substrate(s) and bonding material. In some cases in order to facilitate rapid testing, the bonding material was simply placed on top of a ceramic substrate rather than between two surfaces.

Figures D1 and D2 illustrate two examples of adhesive bonding to a ceramic substrate. Figure D1 shows a smooth layer of adhesive on the ceramic substrate. The adhesive in this case contained a soda-lime glass powder with a thermal expansion coefficient of 85 x 10_{-7}°C^{-1} which is close to that of the substrate 80 x 10^{-7}°C^{-1}. Figure D2, however, illustrates a case of dissimilar coefficients of thermal expansion for the glass powder (100 x 10^{-7}°C^{-1}) and the mullite substrate (45 x 10^{-7}°C^{-1}). A discussion of the SEM characterization used to confirm these findings is given the following section.

Acceptable bonds were achieved with adhesives containing equal amounts (by weight) of glass powder, sodium nitrate and glycerol. When more sodium nitrate or glycerol was used it appeared that excessive heating of the adhesive occurred. This heating is characterized by porosity within the glass bond and subsequent reduction in strength. Gas evolution from overheating of the coupling agent(s) in the adhesive appears to have caused this phenomenon. Figure D3 illustrates an example of reducing the amount of sodium nitrate and glycerol in the adhesive mixture. In this case, exposure to microwaves did not heat the mixture up to the temperature required for satisfactory bonding (see Figure D3). The black areas result from the carbonization of glycerol, while the white sections do not reveal the glass phase as seen in Figures D1 and D2. These observations suggest a critical adhesive composition is required for acceptable bonding.

Based on the results of these preliminary tests, a suitable composition of adhesive components was identified. For all subsequent tests equal amounts of glass powder, sodium nitrate and glycerol were used. The glass powder was a TV solder type (no. 1 in Table D3), while two grades of alumina (nos. 1 and 2) were used as substrates. Figures D4 and D5 illustrate examples of bonding rod (99% Al_2O_3) and plate (96% Al_2O_3) respectively. Various combinations of substrate and thermal insulation and different positions in the microwave applicator were investigated. These tests included: placement of the substrate/adhesive assembly on top of a block of ceramic fibre insulation and covering the assembly with a perforated porcelain crucible; placement in an insulated alumina crucible filled with -Al_2O_3 powder; placement on top of -Al_2O_3 disks. In terms of bonding the best results were obtained with the arrangement provided uniform and direct microwave heating of the two ceramic substrates and avoided unwanted contamination of the bond. The size and shape of ceramic substrates was also investigated. It was observed that rods

FIGURE D1

GLASS FRIT AND CERAMIC SUBSTRATE WITH SIMILAR THERMAL EXPANSION COEFFICIENTS

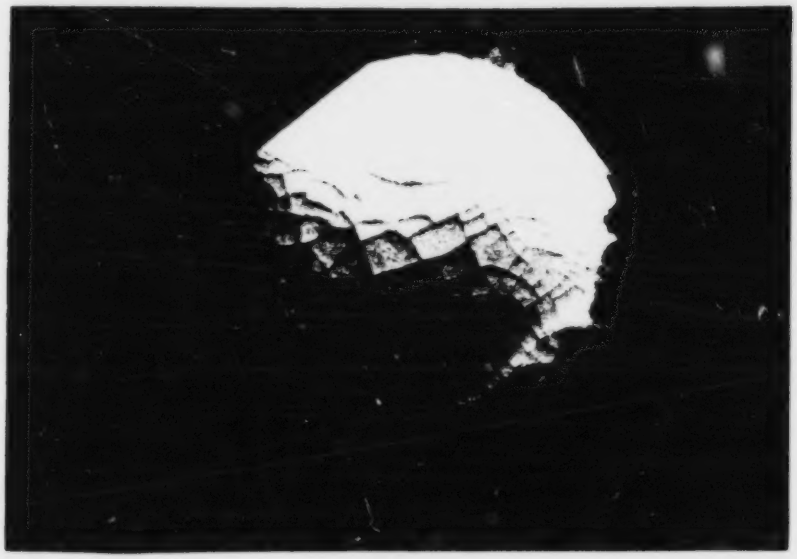


FIGURE D2

GLASS FRIT AND CERAMIC SUBSTRATE WITH DISSIMILAR THERMAL EXPANSION COEFFICIENTS

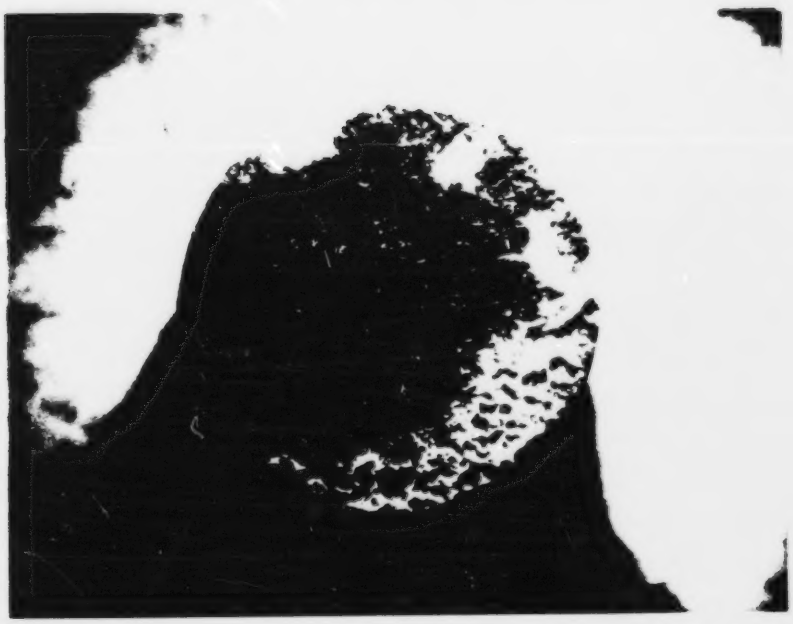


FIGURE D3

CARBONIZATION OF ADHESIVE DURING MICROWAVE HEATING

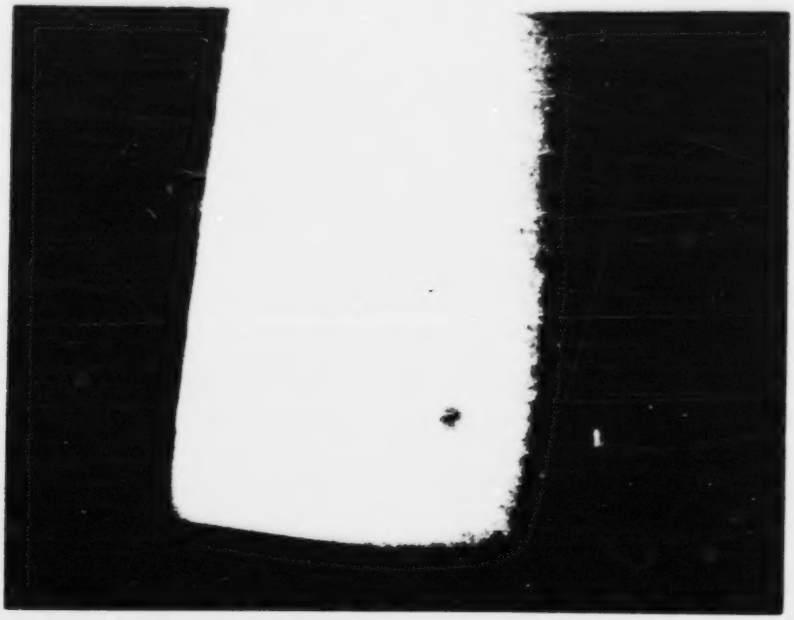


FIGURE D4

MICROWAVE BONDING OF ROD CERAMICS

FIGURE D5

MICROWAVE BONDING OF PLATE CERAMICS

1.25 cm in diameter and 1.25 cm long could not be bonded effectively. The low thermal conductivity and large size of the ceramics appears to be preventing uniform bonding.

Several arrangements (setups) were investigated for microwave heating of substrates. Figure D6 illustrates a typical arrangement. Effective bonding occurred using alumina plates 0.5 mm thick. Plates with the following surface area were tested for bonding:

5 x 5 = 25 sq cm; 1.9 x 1.9 = 3.6 sq cm; 0.6 x 2.2 = 1.32 sq cm

Good bonding was obtained for the smallest size. For the larger plates, effective but non-uniform bonding occurred throughout the samples. Also, most often, the plates cracked at several locations. Good bonding was also obtained between alumina 1.2 cm diameter discs (less than 1.0 cm thick).

The duration required for bonding alumina plates/discs was of the order of 10-15 minutes. The forward and reflected microwave powers were monitored during each test. Typical power curves are shown in Figure D.7 and D.8. Input power was about 900 W. As evident from the figures, the absorbed (forward) microwave power increases with time until, after 5 minutes, absorption becomes optimum. At this point glowing is generally observed. This state lasts for two minutes after which the reflected power starts to increase. The microwave power is then removed and the sample is left to cool naturally inside the insulation.

Temperature measurements were made only after the microwave power was removed. A thermocouple was used in all measurements. Although not exact, temperatures indicated in this report are near the maximum that the sample reached.

Characterization

Scanning electron microscopy (SEM) was mainly used to evaluate the ceramics bonding. Through SEM the adhesive-ceramic interface can be examined, cracks and other defects can be detected, and different phases present can be identified. In addition, energy dispersive x-ray analysis can be undertaken to identify the chemical composition at different key spots near the ceramic-adhesive interface.

Mullite ceramics bonded by either a high melting point soda lime glass or a low melting point solder glass were evaluated using SEM. Figures D.9 and D.10 show the SEM micrographs of the ceramic bond for both glasses.

It is clear from Figures D.9 and D.10 that the bonding glass phase is cracked in both cases. These cracks are due to the large difference in thermal expansion between the mullite ceramic and the glass phase (refer to Tables D.1 and D.2). Because the thermal expansion difference is larger between the mullite and the low melting point glass, more cracks were expected to occur in the bond between these two materials than in the bond between the mullite and the high melting point glass. However, as shown in Figures D.9 and D.10, the

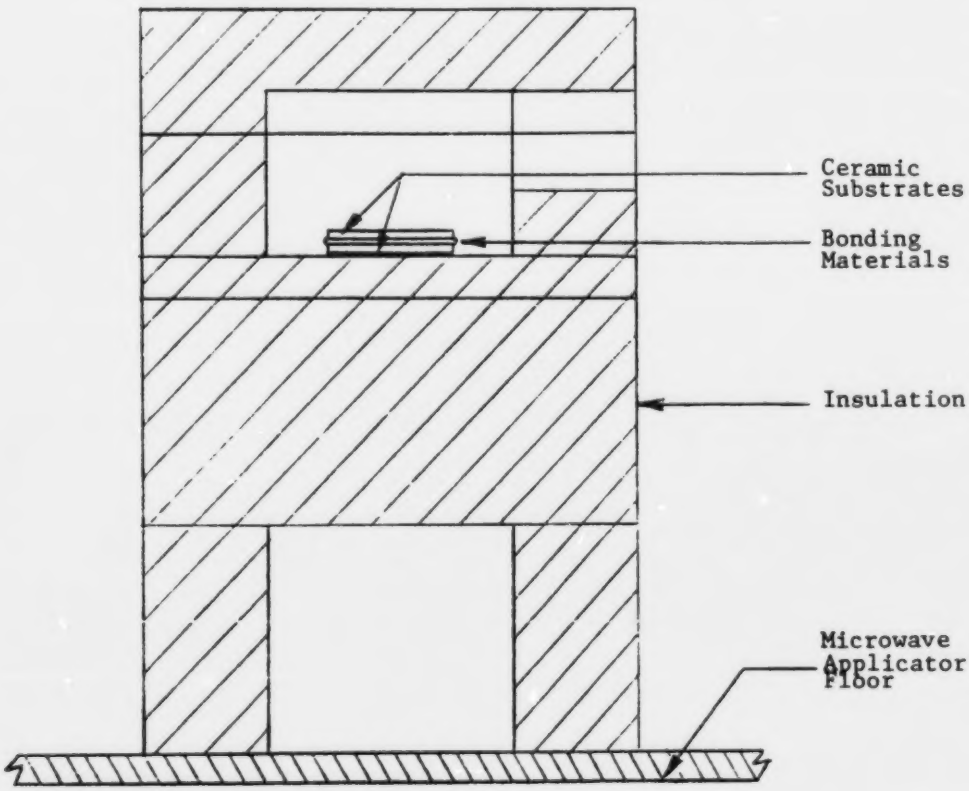


Figure D.6

Typical Arrangement of Ceramic Substrates and
Insulated Enclosure inside Microwave Applicator

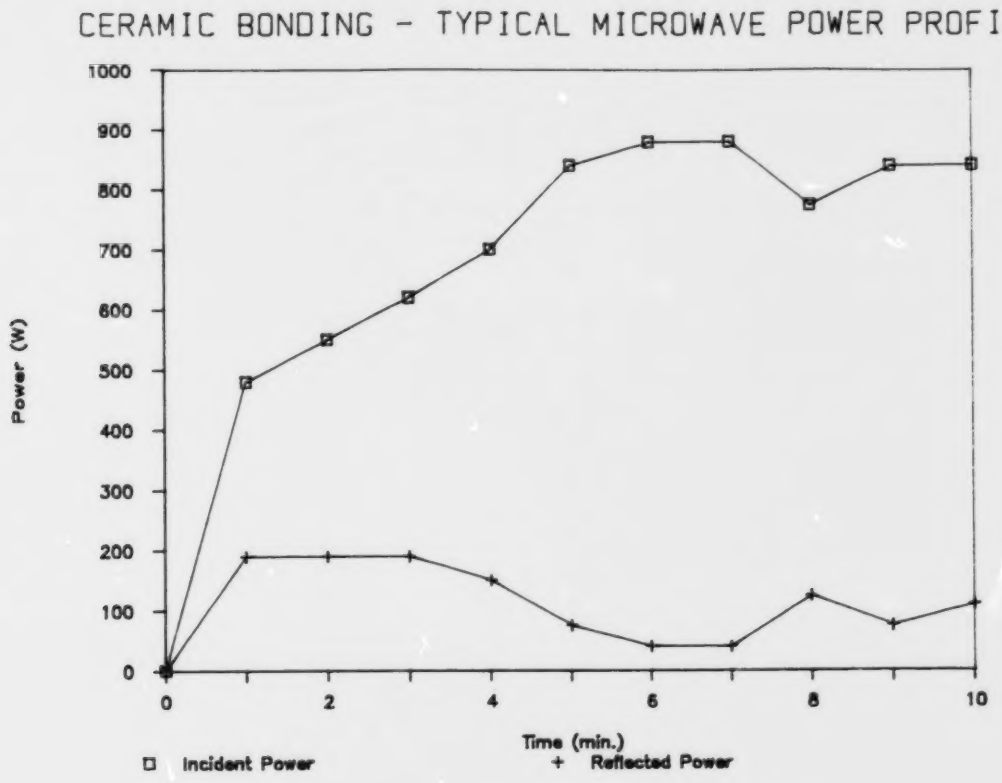


Fig. D.7 – Microwave Power vs. Time

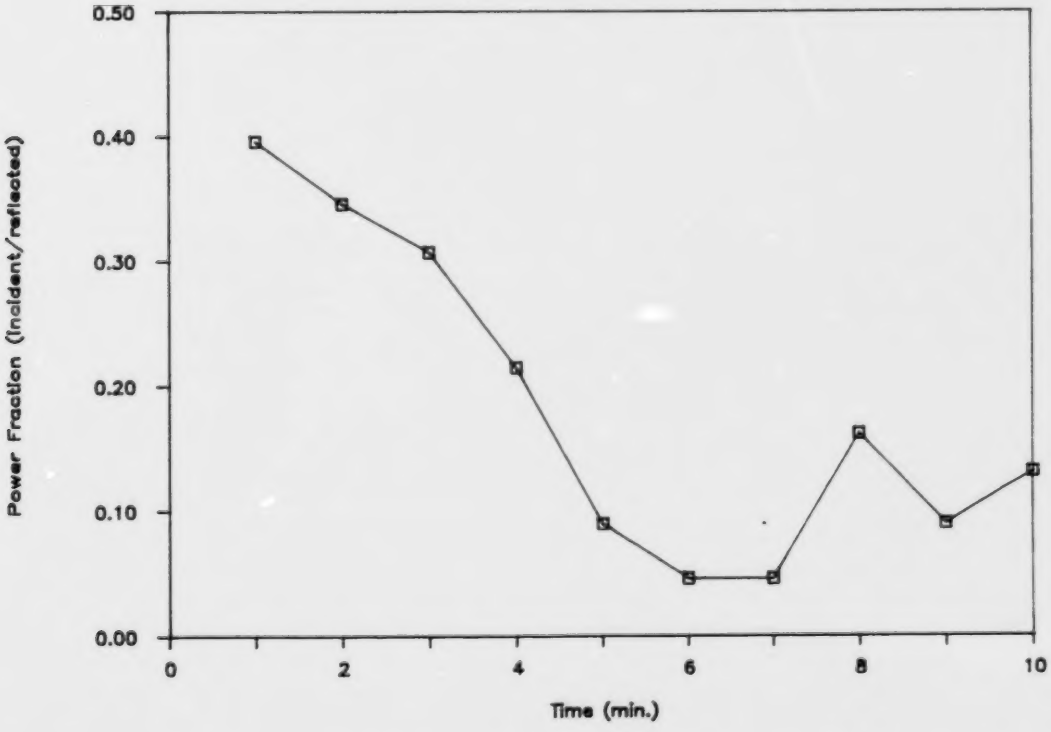
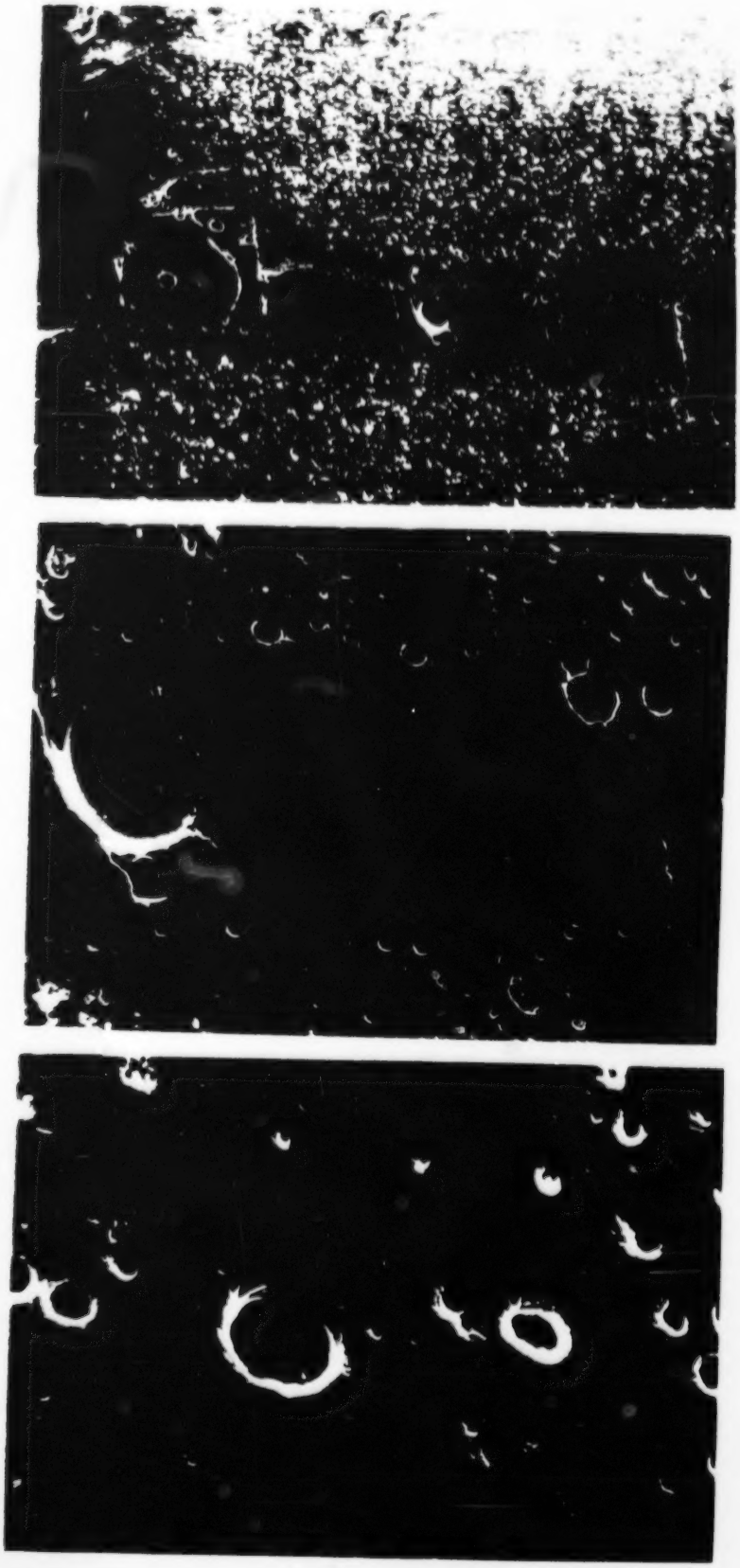


Fig. D.8 – Microwave Fraction vs. Time

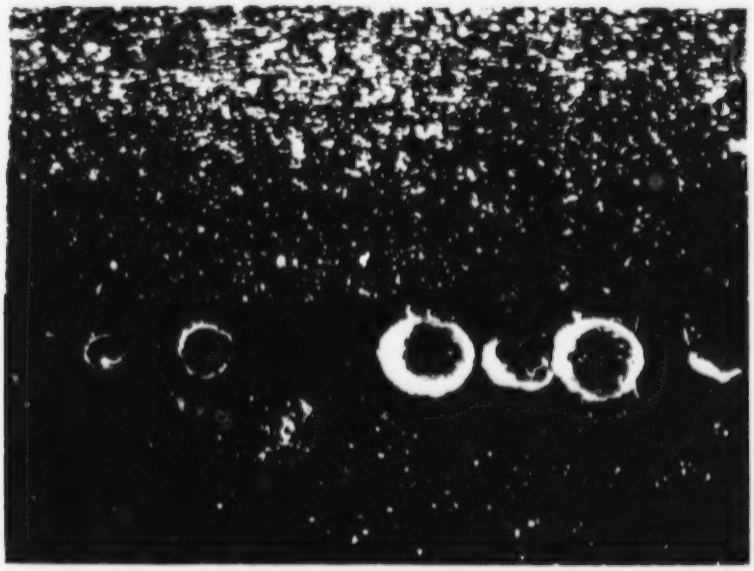


(a)

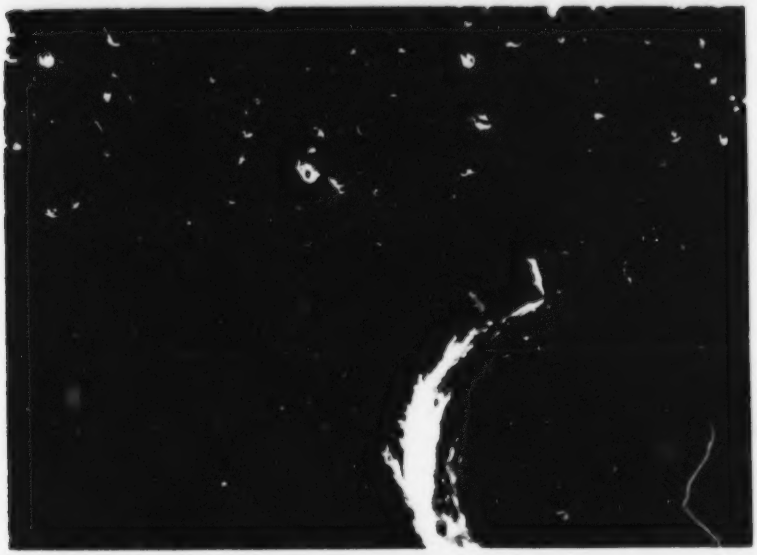
(b)

(c)

Figure D.9
SEM Micrographs of Interface and
Cracks in Glass Bond



(a)



(b)

(c)

Figure D.10
SEM Micrographs of Interface and
Cracks in Glass Bond

reverse effect occurred. A possible explanation to this observation is the fact that during microwave heating, the melting point of the glass was exceeded allowing some constituents to evaporate and/or diffuse into the ceramic. The remaining glass phase could possibly have a thermal expansion closer to that of mullite than it had initially.

Figures D.9 and D.10a and b also show the presence of large bubble-like structures within the bonding glass phase. This is an indication of trapped gases. Most likely these gases are a result of the decomposition of the glass phase due to excessive heating. Because the bond shown in Figure D.9 contains a high melting point glass, the number of bubbles in the glass phase is much less than that in the case of the low melting point glass (shown in Figure D.10).

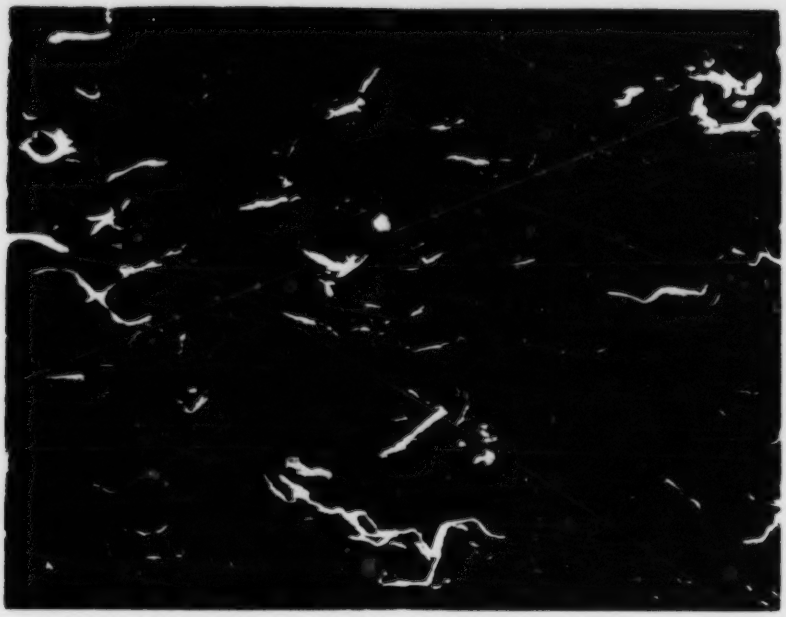
The glass-ceramic interface shown in Figure D.9 has many voids in contrast to the same interface shown in Figure D.10. In the latter case it is clear that some diffusion has occurred (Figures D.10b and D.10c). Not only did the glass phase diffuse into the ceramic, but it also appears that some ceramic particles diffused into the glass. Such diffusion is not evident in the case of the high melting point glass. Because of the presence of voids at the glass-ceramic interface and the absence of diffusion bonding, such a bond is expected to be much weaker than that of mullite bonded by a low melting point glass.

The preliminary evaluations suggested that bonding ceramics with a higher thermal expansion (than mullite) using the low melting point glass should be attempted. Alumina ceramics, with a thermal expansion of 80 x 10^{-7} $°C^{-1}$ were chosen for that purpose.

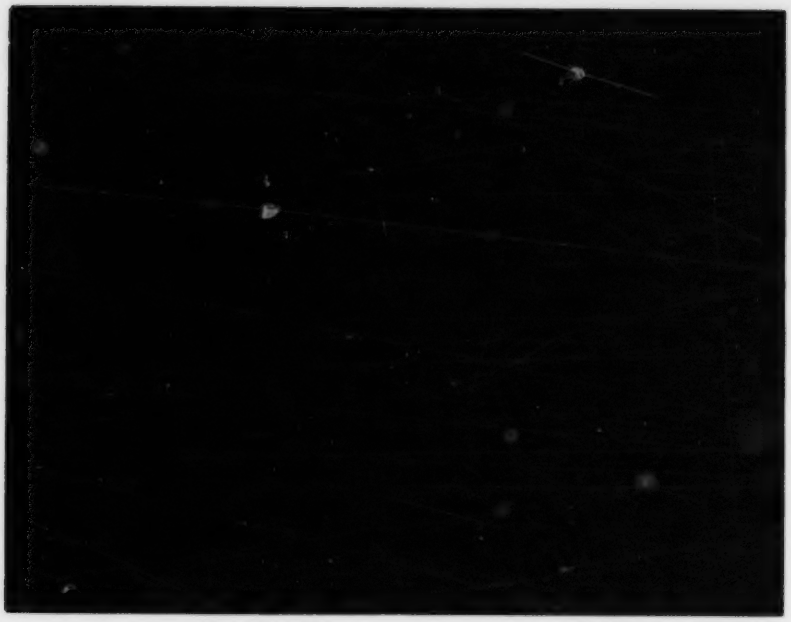
Figure D.11 shows an SEM micrograph of an alumina-glass-alumina interface. Again, diffusion bonding is evident along the entire interface. The three different shades indicate the glass phase (light shade), ceramic phase (dark shade) and mixed phase (medium shade). Diffusion bonding was confirmed by an energy dispersive x-ray analysis (EDX) at several spots within the materials. Figure D.12b shows a map of elemental lead (Pb) in the bond area shown in Figure D.12a. Since the starting alumina ceramic is about 99% pure, only minor impurity traces are expected to be detected in the uncontaminated ceramic. For many reasons, lead is seldom present as an impurity in alumina. It is clear from the micrograph of Figure D.12b that there is considerable lead diffusion in the ceramic. In addition to lead, a general EDX analysis was undertaken at three different locations near the bond interface. Table D.5 summarizes the elements present within the bonding material, at the ceramic-adhesive boundary and at 100 microns from the interface. Clearly several components of the glass phase have diffused as far as 100 microns into the alumina ceramic.

FIGURE D11

SEM MICROGRAPH OF ALUMINA-GLASS-ALUMINA INTERFACE (GLASS PHASE-LIGHT; CERAMIC PHASE-DARK; MIXED PHASE - MEDIUM)



(a) BOND AREA



(b) DIFFUSION OF LEAD INTO CERAMIC SUBSTRATE

FIGURE D12

ENERGY DISPERSIVE X-RAY ANALYSIS OF BOND AREA

Table D.1

RELEVANT PROPERTIES OF CERAMIC SUBSTRATES USED IN BONDING TESTS

Material	Composition	Density g/cm^3	Thermal Conductivity $Wm^{-1}K^{-1}$	Thermal Expansion Coeff $10^{-7}°C^{-1}$	Dielectric Const 1 MHz	Dissipation Factor 1 MHz
Alumina 1	Al_2O_3	3.85	0.336	80	9.7	0.0001
Alumina 2	Al_2O_3, MgO,SiO_2	3.72	0.21	78	9.0	0.0002
Mullite	$3Al_2O_3 \cdot 2SiO_2$	2.5	0.025	45	6.5	0.004

TABLE D.2

GLASS POWDER PROPERTIES

Glass	Softening Point (°C)	Thermal Expansion Coefficient ($\times 10^{-7}$ °C^{-1})	Density (g/cm^3)	Dielectric Constant (1 MHz, 25°C)	Loss Factor (1 MHz, 25°C)
Soda Lime	730	85	2.47	7.3	0.08
Solder Glass	370	100	6.56	22.8	0.016

TABLE D.3

MICROWAVE HEATING OF POTENTIAL BONDING MATERIALS

Sample Description	Maximum Temperature* deg. C	Observations
1. nylon fibre	> 290	melting: no bonding to crucible
2. plastisol (PVC paste)	> 209	burning: weak bonding to crucible
3. PVC film	> 69	no melting
4. solder (resin core)	> 90	no melting
5. Coupling agents:		
(a) silicon carbide powder	> 119	no melting
(b) beta-alumina (β-Al_2O_3) powder	> 325	no melting
(c) sodium nitrate ($NaNO_3$)	> 46	no melting
(d) glycerol	> 290	decomposed; 550-700 W for 5 minutes
6. Glass I mixtures:		
(a) Glass 1 (soda/lime microspheres)	> 73	no melting
(b) glass/beta-Al_2O_3 (1:1 by wt)	> 420	no melting; ~850 W for 10 minutes
(c) glass/beta-Al_2O_3 (3:2 by wt)	> 1000	trace melting; ~800 W for 2 minutes
(d) glass/$NaNO_3$/glycerol/water (2:2:14:1 by wt)	> 1000	glass melting; ~900 W for 3 minutes
(e) glass/$NaNO_3$/glycerol (2:1:2 by wt)	> 500	crusting; very weak bonding to crucible ~700 W for < 4 minutes
(f) glass/$NaNO_3$/glycerol (3:1:3 by wt)	> 1000	glass melting; 750-950 W for 5 minutes
(g) glass/$NaNO_3$/glycerol (4:1:4 by wt)	> 1000	glass melting; 750-850 W for 6 minutes
(h) glass/glycerol/water (1:1:1 by wt)	> 220	no melting; 650-800 W for 5 minutes
7. Glass II (pyrex glass powder)	> 116	no melting

*sample temperature after ~5 minute microwave exposure (< 1000 forward power) except where otherwise noted.

TABLE D.4

PRELIMINARY BONDING TESTS

	Bonding Material	Substrate	Max Temperature* deg C	Observations
1.	nylon fibre	porcelain	> 290	weak bond 800-1000 W for 10 minutes
2.	plastisol (PVC paste)	porcelain	> 717	no bond; bond mat'l vaporized 450-750 W for > 11 minutes
3a	Glass I (soda/lime microspheres)	beta-alumina (β-Al_2O_3)	> 862	excellent bond 700-900 W for 5 minutes
3b	as above	beta-Al_2O_3 to copper	> 712	good bond 500-700 W for 10 minutes
3c	as above	beta-Al_2O_3 to porcelain	> 1000	good bond; alumina fracturing 650-800 W for 10 minutes
4.	Glass I mixtures:			
4.1	beta-Al_2O_3/glass/sodium nitrate ($NaNO_3$)/glycerol (6:4:5:5 by wt)	porcelain	> 300	weak bond; potential apparent ~850 W for 2 minutes
4.2	as above less $NaNO_3$	porcelain	> 200	no bond 850-1000 W for 10 minutes
4.3	as above less glycerol	porcelain	> 315	no bond 600-850 W for 15 minutes
4.4a	glass/$NaNO_3$/glycerol/water	porcelain	> 624	no bond; potential apparent 550-700 W for 6 minutes
4.4b	as above	magnesia	> 193	no bond; substrate role significant ? 450-650 W for 10 minutes
4.5a	glass/$NaNO_3$/glycerol (1:1:1 by wt)	magnesia	> 800	excellent bond 600-1000 W for 5 minutes
4.5b	as above	porcelain	> 1000	excellent bond ~800 W for 5 minutes
4.5c	as above	porcelain to porcelain	> 950	excellent bond ~900 W for 10 minutes
4.6	glass/$NaNO_3$/glycerol (2:1:2 by wt)	porcelain	> 1000	excellent bond 750-900 W for 8 minutes
4.7	glass/$NaNO_3$/glycerol (3:1:3 by wt)	porcelain	> 1000	fair bond; partial glass melting 750-950 W for 5 minutes
4.8	glass/$NaNO_3$/glycerol (4:1:4 by wt)	porcelain	> 1000	excellent bond 700-800 W for 8 minutes
5.	Glass II (pyrex glass powder)	beta-Al_2O_3	> 1000	excellent bond 650-750 W for 10 minutes
6.	aluminum foil	beta-Al_2O_3 to beta-Al_2O_3	> 830	weak bond

* sample temperature following microwave exposure as noted.

TABLE D.5

ELEMENTAL ATOMIC PERCENT

Element	Bonding Material	Ceramic/Glass Interface	100μmFrom Interface
Al	30.7	45.0	98.5
Si	6.4	5.6	--
Zn	34.1	35.8	0.56
Ba	3.7	2.5	0.29
Pb	25.1	11.1	0.65